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<p>(54) Title: CROSSLINKABLE POLYMERS  (57) Abstract  Silane-modified polymers are disclosed together with their use in adhesive compositions. The polymers are unsaturated, i.e. contain unsaturated carbon-carbon bonds in the polymer backbone or groups pendant therefrom.</p>		

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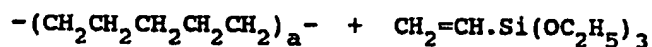
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CROSSLINKABLE POLYMERS

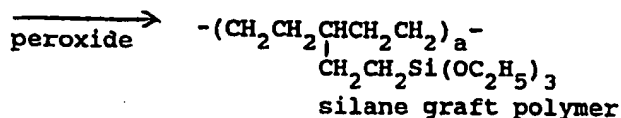
The present invention relates to novel silane  
 5 grafted unsaturated polymers and to hot melt adhesives,  
 sealants, foam gaskets and moulded articles prepared  
 therefrom.

Silane grafted homo- and co-polymers are widely  
 used for the preparation of cable jacketing, wire  
 10 insulation and piping and have been suggested for use as  
 spacers in laminate materials. The preparation of such  
 materials is described in for example US-A-3646155,  
 GB-A-1286460, GB-A-1347426, GB-A-1406680, GB-A-1450934  
 and GB-A-1542543. US-A-3646155, for example, describes  
 15 the production of such material by reaction of  
 polyethylene with an unsaturated silane, e.g. vinyl  
 triethoxysilane, in the presence of a peroxide initiator  
 to produce the silane grafted polymer. A catalyst, for  
 example dibutyl tin dilaurate, is incorporated into the  
 20 grafted polymer which is then formed into the desired  
 shape. Catalysed hydrolysis and cross-linking of the  
 silane groups occurs to give the hardened end product.  
 The reaction procedure may thus be represented as  
 follows:-

25

(A) Grafting

30



$$5 \quad \begin{array}{c} \text{-(CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{)}_a\text{-} + 3 \text{H}_2\text{O} \\ \text{CH}_2\text{CH}_2\text{Si(OC}_2\text{H}_5\text{)}_3 \end{array}$$

$$\longrightarrow \begin{array}{c} \text{-(CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{)}_a\text{-} + 3 \text{C}_2\text{H}_5\text{OH} \\ \text{CH}_2\text{CH}_2\text{Si(OH)}_3 \end{array}$$
$$\begin{array}{ccc}
 10 & & \\
 & \text{-(CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{)}_a\text{-} & \text{-(CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{)}_a\text{-} \\
 & | & | \\
 & \text{CH}_2\text{CH}_2\text{Si(OH)}_3 & \text{CH}_2\text{CH}_2\text{Si-O-} \\
 15 & \xrightarrow[\text{catalyst}]{\text{silanol condensation}} & \text{O-} \\
 & + & | \\
 & & \text{O} \\
 & \text{CH}_2\text{CH}_2\text{Si(OH)}_3 & \text{CH}_2\text{CH}_2\text{Si-O-} \\
 & | & | \\
 20 & \text{-(CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{)}_a\text{-} & \text{-(CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_2\text{)}_a\text{-}
 \end{array}$$

The product of stage (A) above may also be produced by copolymerisation of ethylene with a suitable trialkoxysilyl monomer, e.g. 4-(triethoxysilyl)-  
25 but-1-ene. References hereinafter to silane-grafted or silane-modified polymers include such silane side chain materials produced by copolymerisation, which are essentially the same as the materials produced by grafting.

30 While teaching that for storage stability the  
silanol condensation catalyst should be incorporated  
into the silane-grafted polymer only when initiation of  
the cross-linking reaction is desired, Dow Corning  
Limited have suggested in GB-A-1406680 that silane  
35 grafted ethylene-vinyl acetate copolymers may find  
utility in adhesives. In British patent application No.  
8724865 (GB-A-2197326) Swift Adhesives Limited have

however suggested the use of a silane-grafted medium range molecular weight ethylene-vinyl acetate copolymer as the base for cross-linkable hot melt adhesive systems (which can either be formulated as single compositions  
5 containing the grafted copolymer together with the condensation catalyst or as dual compositions, one containing the grafted copolymer and the other the catalyst) which are particularly suitable for use in product assembly, for example in the furniture and  
10 automobile industries.

It has also been proposed to use silane-grafted hydrogenated, i.e. saturated, styrene-olefin-styrene block copolymers in sealant compositions and moulded articles, for example in EP-A-240044, JP-A-59102931 and  
15 JP-A-58132032.

The present invention is based on the recognition that silane modified unsaturated polymers can combine the known desirable characteristics of the basic polymers and the rapid, room temperature or moderately  
20 elevated temperature curing properties of silane side chains.

Accordingly in a first aspect the invention provides silane modified (including silane grafted) unsaturated polymers as hereinafter defined. For  
25 convenience these materials will be referred to as SGPs.

In a related aspect the invention provides crosslinked (e.g. cured) silane modified unsaturated polymers and articles made therefrom.

The term "unsaturated polymer" designates a polymer  
30 having unsaturated carbon - carbon bonds, e.g. double bonds, situated along the polymer backbone or in groups pendant therefrom. Generally at least 0.5% of the carbon-carbon bonds will be carbon-carbon double bonds and preferably at least 1%. However it is preferred  
35 that not more than 50%, especially not more than 35%, particularly not more than 25%, of the bonds be double bonds as higher levels will make silane grafting

difficult. Where a block copolymer is referred to these figures apply to the relevant block of the copolymer, and not to the polymer molecule as a whole. For example, in a styrene - isoprene - styrene block copolymer it can be calculated that approximately one in four of the polymer backbone carbon - carbon bonds will be unsaturated, i.e. an overall degree of unsaturation of 20%.

Suitable unsaturated rubbers include the following:

(1) (Monoalkenyl arene)-(conjugated diene)-(monoalkenyl arene) block copolymers

These include, for example, styrene- conjugated diene - styrene block copolymers such as styrene - isoprene - styrene (SIS) and styrene - butadiene - styrene (SBS). Typical commercially available materials are Kraton 1107 (SIS) and Kraton 1102 (SBS) available from Shell. Since a higher degree of chain extension than normally acceptable may occur when SBS is subjected to a silane grafting reaction, it is preferred that a lower molecular weight SBS be used when the final SGP is to be produced by grafting. It is possible that the chain extension is hindered in polymers such as SIS by the presence of a methyl group adjacent to the double bond; accordingly it is preferred that the styrene-olefin-styrene block copolymer contain an olefin monomer having a nonreacting sterically hindering group, e.g. C<sub>1-4</sub> alkyl group, present on at least one of the carbon atoms participating in the carbon-carbon double bond.

(2) (Monoalkenyl arene)-(conjugated diene) random copolymers

This category includes the well known styrene-butadiene random copolymers (SBR).

### (3) Nitrile rubbers

These polymers are copolymers of one or more unsaturated nitriles with one or more conjugated dienes.

5 The diene is commonly butadiene although isoprene, 2-ethyl-butadiene, 2,3-dimethyl-butadiene and piperylene have been used. The nitrile is generally acrylonitrile although again other unsaturated nitriles can be used. A typical example of a butadiene-acrylonitrile rubber is  
10 Breox 1442 available from BP.

### (4) Polychloroprenes

This class of unsaturated polymers comprises  
15 polymers of 2-chlorobutadiene such as Neoprene AC available from Du Pont.

### (5) Butyl rubbers

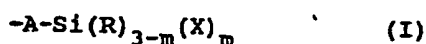
20 This class includes copolymers of isobutylene and isoprene, generally with only a small amount of isoprene and typically containing 50 isobutylene units per isoprene unit. The polymer is distinguished from polyisobutylene in that the latter contains  
25 substantially no double bonds along the polymer backbone. This class also includes chlorinated butyl rubbers prepared by chlorination of the original butyl rubber. It is preferred that the butyl rubbers for use in the present invention are at least 0.5% unsaturated  
30 as defined above, more preferably 1% unsaturated and conveniently not more than 5% unsaturated. It will be seen that, like the polyisoprene block of SIS, butyl rubbers have a nonreactive methyl group adjacent to the double bond which may hinder chain extension.

35

The invention is conveniently applicable to unsaturated polymers prepared from a conjugated diene or

containing a conjugated diene as one of the comonomers. Thus the carbon-carbon double bonds will be present in the backbone or, when present in a pendant group, will be separated from the backbone by one carbon-carbon single bond. It is preferred that the unsaturation be present in the polymer backbone and that any pendant groups be saturated.

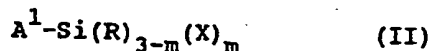
In the SGPs according to the invention, the silane side chain is conveniently of general formula (I)



wherein A represents an optionally substituted divalent organic radical, preferably an optionally substituted alkylene, alkyleneoxy, alkylene-phenylene, or alkylene-oxy-alkylene chain; X represents a leaving group displaceable by hydrolysis, conveniently a halogen atom (e.g. chlorine) or a group  $\text{R}^1\text{O-}$  or  $\text{R}^1\text{COO-}$  where  $\text{R}^1$  is a  $\text{C}_{1-10}$ , preferably  $\text{C}_{1-4}$ , alkyl or alkoxyalkyl group; m is 1, 2 or 3, preferably 2 or 3; and R represents a blocking group not displaceable by hydrolysis, for example a  $\text{C}_{1-4}$  alkyl group.

As mentioned above the silane side chains may be present in a monomer which is copolymerised to produce the SGP.

The SGP component for inclusion in the adhesive compositions of the invention may also be prepared by reacting the polymer (or blend thereof) with an unsaturated silane of formula II

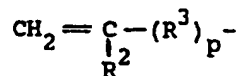


(where  $\text{A}^1$  represents an ethylenically unsaturated organic group corresponding to the divalent group A in formula I and R, m and X are as defined above) in the presence of a catalyst, conveniently a peroxide catalyst, for example using the reagents and conditions



specified in the literature.

In formula II, A<sup>1</sup> conveniently represents a group of formula



where p is 0 or 1; R<sup>2</sup> represents hydrogen or C<sub>1-4</sub> alkyl; and R<sup>3</sup> represents a C<sub>1-10</sub> straight, branched or cyclic alkylene group, a phenylene group, a carbonyloxy group, a carbonyloxy(C<sub>1-10</sub> alkylene) group, a (C<sub>1-10</sub> alkylene)carbonyloxy group or a (C<sub>1-10</sub> alkylene)carbonyloxy(C<sub>1-10</sub> alkylene) group, optionally carrying pendant glycidoxo groups. Such compounds are described by Dart Industries in GB-A-1347426.

Particularly preferably however A<sup>1</sup> represents a C<sub>2-5</sub> monoalkenyl group, such as vinyl or allyl, or a (C<sub>2-3</sub> alkenyl)carbonyloxy(C<sub>2-3</sub> alkylene) group, such as a gamma-methacryloxy propyl group, and particularly preferred unsaturated silanes of formula II include vinyl trimethoxy silane, vinyl triethoxy silane and gamma-methacryloxypropyl trimethoxy silane.

Unsaturated silanes of formula II are known or may be prepared by conventional methods.

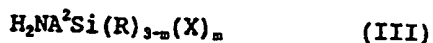
The silane grafting reaction is conveniently effected at a temperature of at least 140°C, preferably between 150°C and 250°C, and may be performed in conventional apparatus such as a Ko-Kneader.

The catalyst used in the preparation of the SGPs is preferably a free-radical generating compound such as for example benzoyl peroxide, dicumyl peroxide or other catalysts referred to in the literature, e.g. in US-A-3646155. The free radical generator may conveniently be used in a concentration of about 0.01 to 3% relative to the weight of polymer used.

A third method of producing the SGP may be appropriate when the polymer contains groups or atoms which will prevent the conventional grafting reaction

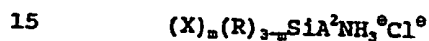
from working effectively, for example the chlorine atoms in polychloroprenes which will generate HCl. This method will involve the use of an aminosilane of general formula III

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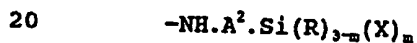
wherein  $\text{A}^2$  is an optionally substituted divalent organic radical as defined above for A, and R, X and m are as defined above. Two equivalents of silane will be required for each equivalent of silane to be introduced into the polymer as one equivalent will combine with the HCl to form

10



15

while the second equivalent is introduced into the polymer as an



20

group.

The silane side chain need only constitute a minor part by weight of the SGP, e.g. up to 20%, generally 0.1 to 10%, preferably 0.5 to 6% and especially preferably about 4%.

25

The SGPs of the invention may be used in adhesives including for example both hot melt and solvent based adhesive systems. Thus a further aspect of the invention provides an adhesive composition comprising (a) a silane modified unsaturated polymer as defined above and (b) a catalyst for the condensation of said silane modified unsaturated polymer.

30

As the catalyst for the SGP hydrolysis and cross-linking, a silanol condensation catalyst may be used both in solvent based and hot melt systems. Many

35

such materials are known to the art. Thus suitable catalysts include, for example, metal carboxylates, e.g. dibutyl tin dilaurate, organometallics, e.g. tetrabutyl titanate, organic bases, e.g. ethylamine, and mineral  
5 and fatty acids. Several such compounds are identified for example in US-A-3646155. Among suitable condensation catalysts, organotin compounds, such as dibutyl tin dilaurate are preferred. The catalyst, conveniently makes up from 0.005-0.2%, preferably about  
10 0.02%, of the adhesive composition as a whole.

Where an adhesive according to the invention is to be solvent based it will have the advantage of cross linking at room temperature while nonetheless being a one part formulation. Conventional solvent based  
15 adhesives are either cured by heating or must be two part formulations using a chemical curing process. The solvent based adhesive compositions according to the present invention have significant advantages in terms of convenience of application and curing.

20 As suitable solvents for polychloroprenes and SBR mention may be made of aromatic or aliphatic hydrocarbons with varying proportions of oxygenated solvents such as ketones and esters, i.e. hexane, toluene, methyl ethyl ketone, acetone or (for non-  
25 flammable adhesives) methylene chloride. Solvents for nitrile adhesives include aromatic hydrocarbons, chlorinated hydrocarbons, ketones, esters and nitroparaffins. Solvent based adhesives may also contain tackifying resins (as up to 90% of the total  
30 solids content), plasticisers (up to 80% of solids), fillers (up to 80% of solids) and colourants and stabilisers (generally not more than 10% of solids). Further description of these materials is found hereinafter. The total level of solids in the solvent  
35 can conveniently range from about 10% for a sprayable adhesive to about 95% in sealants.

. Hot melt adhesive systems according to the

invention are preferably based on the block or random copolymers of types (1) and (2) referred to above or on butyl rubbers. It is particularly preferred to use silane grafted styrene-isoprene-styrene in these hot melt adhesives.

The hot melt adhesive systems will desirably contain a plasticiser to improve substrate wetting by the hot melt and to improve flexibility in the cured adhesive. The plasticiser may be for example an ester-based plasticizer (e.g. benzoate plasticizers such as glycol dibenzoate and dipropylene glycol dibenzoate (available as Benzoflex 9-881)) a liquid polyterpene or liquid hydrocarbon plasticizer (such as for example the polyterpene available from Goodyear under the trade name Wingtack 10 and the liquid hydrocarbon available from Exxon under the trade name Escorez 5000), a polybutene plasticizer, a phthalate plasticiser or a process oil such as Shellflex 451 available from Shell. The plasticizer conveniently constitutes up to 80%, preferably 10-35%, of the hot melt adhesive composition.

Polymers having a wide range of molecular weights may be silane grafted to produce the SGPs used for the preparation of the adhesive compositions of the present invention; in general polymers having melt flow indices (MFIs) of from 1 to 2500 may be used and MFIs of 2-1000, especially 5-400 and particularly 10-150, are preferred. By blending polymers having different pre silane grafting MFIs and indeed by blending grafted polymers having different monomer make-up the performance profile of the final adhesive system, for example in terms of wetting, strength, adhesion, flexibility, and ease of application, may be adjusted to suit its intended end use.

The SGP component preferably forms up to 90%, conveniently 10-40%, and especially preferably about 30%, of the hot melt adhesive composition.

In the hot melt adhesive composition of the

invention, SGPs having a 3-membered or longer chain linking the silicon atoms with the polymer backbone will result in a cured adhesive having a generally more open structure than that achieved with only a 2- membered linking chain. The open structure may advantageously permit both a high degree of curing and the inclusion of relatively high concentrations of tackifying resin and other components in the uncured adhesive composition. In this way, the viscosity, tack and melting characteristics of the uncured adhesive may be tailored to particular desired levels, for example to permit the use with the new adhesive of conventional hot melt adhesive melting, mixing and application apparatus.

The hot melt adhesive composition of the invention conveniently also contains further components selected from: antioxidants; tackifying resins; further polymers; and diluents and modifiers.

The tackifying resin component of the hot melt adhesive composition of the present invention may comprise any suitable resin or resin mixture, for example those conventional for hot melt adhesives. The resin or resin mixture should however be selected to achieve the desired balance between compatibility with the SGP and the other components of the adhesive, the melt flow properties of the adhesive as a whole and the specific adhesion to the substrates intended to be bonded with the adhesive. In this respect, suitable tackifying resins may include: aromatic modified resins such as  $\alpha$ -methyl styrene homopolymers or copolymers, e.g. Krystalex F100 ( $\alpha$ -methyl styrene polymer), Krystalex FR75 (a modified  $\alpha$ -methyl styrene copolymer) or Piccotex (a vinyl toluene-  $\alpha$ -methyl styrene copolymer), all three available from Hercules Chemical Co.; aliphatic petroleum hydrocarbon resins; styrene-modified hydrocarbon resins; polyterpene resins; terpene phenolic resins; rosin and rosin esters; reactive resins containing for example acid groups,

hydroxyl groups or silanol groups; and, particularly preferably, alicyclic hydrocarbon resins, e.g. Escorez 5300 (available from Exxon).

5 The tackifying resin will conveniently comprise up to 80%, preferably 10-40%, and especially preferably about 30%-35%, of the adhesive.

10 The hot melt adhesive of the invention preferably contains at least one antioxidant. In this respect, conventional adhesives antioxidants, such as butylated hydroxytoluene (BHT) may be used. A preferred antioxidant is pentaerythritol-tetrakis-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate, which is available under the trade name Irganox 1010 from Ciba-Geigy UK Ltd. of Manchester. The antioxidant will  
15 generally be present in the adhesive at about 0.1-2.5%, preferably 0.5-1%.

The hot melt adhesive system may if desired be formulated as two compositions which are not mixed until the adhesive is melted for application so as to avoid  
20 earlier contact between the SGP and the condensation catalyst. Thus according to a further aspect of the invention we provide a hot melt adhesive system comprising a first composition comprising at least one SGP as defined above and a second composition comprising  
25 a catalyst for the condensation of said SGP, said first and second compositions being packed in separate containers.

The hot melt adhesive composition of the invention preferably also comprises a further polymer or polymer  
30 mixture. The further polymer or polymer mixture, which should not be cross-linkable under the action of the catalyst, will be selected to achieve, inter alia, a balance between compatibility with the catalyst and the other components of the adhesive and the viscosity and  
35 tack characteristics of the adhesive. The further polymers are preferably selected from homo- and copolymers of apolar monomers, such as for example

polyethylene, polypropylene, polybutylene, and SEBS (for example low crystallinity range molecular weight homo-or copolymers, such as that available under the trade name Vestoplast 608 from Hüls (UK) Limited of Manchester, or low molecular weight polyethylene, such as polyethylene AC6 or AC8 available from Allied Chemical Corporation International NV SA of Birmingham) or from copolymers containing polar comonomers such as poly(ethylene-vinyl acetate). Conveniently polymers having MFIs of 1 to 2500, preferably 5-800, more preferably 20-500 and most preferably 150-400 are used. The further polymer conveniently constitutes up to 15%, preferably 1 to 10%, and especially preferably about 5%, of the adhesive of the invention and generally will be present at about half the concentration of the SGP.

The hot melt adhesive composition or system may also contain further components such as diluents or modifiers, conveniently as about 5-40%, preferably about 30%, of the total adhesive. These components may serve to regulate the viscosity and setting speed of the adhesive and may be included to enhance the wicking of the adhesive into the substrates to be bonded. In this respect, conventional diluents and modifiers for hot melt adhesives, such as waxes (e.g. petroleum waxes such as paraffin waxes or microcrystalline waxes such as Okerin 8981 from Astor Chemicals of West Drayton, Middlesex), hydrogenated animal or vegetable fats (e.g. hydrogenated castor oil or hydrogenated tallow), and synthetic waxes, such as Fischer Tropsch waxes may be used.

Where waxes or low molecular weight polyethylenes are used as diluents, they should conveniently have softening temperatures in the range of 50- 120°C. Microcrystalline waxes, Fisher Tropsch waxes and paraffin waxes having softening temperatures in the ranges 65 to 94°C (e.g. 79°C), 110 to 120°C and 54 to 72°C respectively are particularly suitable. A mixture

of low molecular weight polyethylene, such as polyethylene AC6 or AC8, and a microcrystalline wax having a softening temperature of about 90°C, such as Micro 549 available from Holmes Chemical Company of Uxbridge, may also be particularly suitable, especially where the polyethylene and the wax constitute about 5 and about 15% by weight respectively of the adhesive.

Where the hot melt adhesive is formulated as a two part system, the SGP and the catalyst being separately packaged, the optional components can appear in one or both of the separate compositions; the SGP- containing composition will however preferably contain the antioxidant and the tackifier and the catalyst-containing composition will preferably contain a further polymer; the plasticizers, diluents and modifiers may be in either or both compositions. In a two composition system, the catalyst-containing composition particularly conveniently comprises about 99% of polymer compatible with the SGP (e.g. polyethylene, polypropylene or SEBS) and 1% of a catalyst (e.g. dibutyl tin dilaurate).

Where the hot melt adhesive of the invention is formulated as a single composition it will advantageously be packaged in water-tight containers, for example aluminium cartridges, which containers advantageously will also include a desiccant, for example a sachet of silica gel at the end of a cartridge for a hot melt adhesive applicator. Thus, according to a further aspect of the invention we provide a hot melt adhesive applicator cartridge comprising a water-tight container containing therein a desiccant and a hot-melt adhesive composition, said composition comprising an SGP as hereinbefore defined and a catalyst for the condensation thereof.

Besides the hot melt components discussed above, it may be desirable to incorporate into the hot melt adhesive a colouring agent, for example a whitener such



as titanium dioxide. Such colouring agents are particularly readily dispersed within the hot melt adhesive if introduced as solid dispersions in a polymer compatible with the SGP. In use, the adhesive of the present invention will be heated to melting, generally to 100-200°C preferably about 110-170°C, mixed (e.g. in a cartridge loaded applicator or by the mixing in a mixer head of the two compositions of a two composition system) and applied to the substrates to be bonded, generally in a film thickness of up to about 3 mm, preferably up to about 1 mm, although this can be achieved by applying a larger amount and scraping off the excess. The adhesive characteristics of the system should be sufficient to maintain a bond between the substrates while the curing of the SGP component by hydrolysis and cross-linking occurs.

For the hydrolysis of the SGP, water is required. In general, the necessary water can be supplied by ambient moisture. However, if desired, the hot melt adhesives according to the invention may contain further components which gradually release moisture into the system, for example fillers with surface-bound moisture or moisture filled polymer microspheres such as those sold as paint opacifiers by Rohm and Haas Company under the trade name ROPAQUE OP-62 (see EP-A-119054 of Rohm and Haas).

The hot melt adhesive of the invention may be used in most applications where hot melt adhesives have been used and where full bonding strength is not required immediately after the application of the adhesive. The adhesive of the invention is thus particularly suited to use in product assembly (for example in the furniture and automobile industries), packaging and labelling.

Thus according to a further aspect of the invention we provide the use of the hot melt adhesive composition and system of the invention in product assembly.

Because of the silane cross-linking reaction, the

adhesive of the invention is capable of chemically bonding to the surfaces of certain substrates to produce an enhanced adhesive effect. Thus the adhesive of the present invention is particularly suitable for the bonding of cellulosic and siliceous substrates, for example paper and glass.

The SGP and catalyst components in both the hot melt and solvent based adhesive of the present invention may be selected to achieve particular desired characteristics, for example rate or controllability of curing, and by varying the monomer make-up and the MFI of the polymer precursor for the SGP, and by utilizing blends of SGPs, the formulation characteristics (such for the adhesive may be controlled to give a readily processable material.

In a particularly preferred embodiment of the invention, further organic components, such as for example fillers, tack and viscosity modifiers, plasticizers and colorants can be bonded onto the cross-linked lattice produced by curing the silane grafted polymer by using for such components compounds containing, or chemically modified to contain, silanol, alcohol, amine or thiol groups. The use of such compounds is particularly advantageous since although they are unreactive towards the SGP in the adhesive composition before the application of the adhesive, on application they are able to bond to the silanols produced in the hydrolysis reaction and thereafter will be chemically bound into the cured adhesive. In this way where such components are polyfunctional, i.e. contain two or more such groups on each molecule, the components may act as intermediaries in the cross-linking and by becoming part of the cross-linked lattice may modify the physical properties of the cured composition. However even when such components are monofunctional they may bond to the silane grafted polymer so reducing any tendency they may have to leach

out of the cured composition even under adverse conditions. In this regard mention may be made in particular of glycerol esters of resins, polyamines, diols, polyethylene glycols, hydroxylated waxes and the like.

The use of such reactive compounds may be particularly advantageous in increasing the thermal stability of the cured composition or where the optional component is capable of discoloring or otherwise damaging the substrate or where loss of the component would cause the adhesive bond to be modified undesirably, e.g. where it would deteriorate.

The SGPs according to the invention are also of particular use in the formulation of pressure sensitive adhesives, and a further aspect of the invention provides a pressure sensitive adhesive composition, characterised in that it comprises a cross-linkable, silane modified unsaturated polymer as herein defined.

Pressure sensitive adhesives are distinguished by their surface tack levels, which can readily be measured in many ways, for example using the rolling ball or loop tack tests. However, it may be noted that, unlike sealants, which on curing should retain substantially no surface tack even though they may contain tackifying resins, pressure sensitive adhesives must on curing e.g. for 5 to 17 days retain some level of surface tack even if only a relatively low level such as that exhibited by the repositionable notes recently put onto the market by 3M under the trade name POST-IT. Generally, a pressure sensitive adhesive would be expected to have a score of less than 10 cm, more usually less than 5cm, e.g. 2 cm, in the rolling ball test. In the loop tack (FTM No 9) test method, pressure sensitive adhesives would generally score greater than 1 Newtons/25 mm, e.g. about 10 N/25 mm. Thus in another aspect of the invention we provide a pressure sensitive adhesive composition scoring greater than 1 N/25mm in the loop tack (FTM No

9) test and comprising an adhesive composition according to the invention cured to effect cross linking of said silane modified polymer.

5 The SGPs according to the invention are also useful in the production of hot melt foam gaskets. They will be formulated as described above and can be applied using known foam gasket technology, for example the Foammelt available from Nordson Corp.

10 The SGPs according to the invention will also be of use in sealants and moulded articles which would normally require a heat or two part chemical curing process. The silane cross-linking ability of the SGPs allows moisture curing at room temperature while retaining the desirable properties of the base polymer, 15 e.g. fire retardancy (Neoprene), solvent resistance (nitrile) and low gas permeability (butyl rubber). In moulded articles such as tyres, shoe soles, cable sheathing, etc., the article may be removed from the mould and cured elsewhere rather than heat cured in the 20 mould itself, thus freeing the mould and eliminating a production bottleneck.

It has been found that silane grafted styrene-isoprene-styrene forms a particularly tough and flexible material upon curing. Accordingly the invention also 25 provides moulded articles formed from the silane grafted unsaturated polymers according to the invention, preferably silane grafted styrene-isoprene-styrene.

The invention is illustrated by the following non-limiting Examples.

30

#### Example 1

##### Preparation of silane grafted SIS block copolymer

35 100 parts by weight Kraton 1107 (styrene-isoprene-styrene block copolymer) is reacted with two parts by weight of vinyl trimethoxy silane using 0.25 parts by

weight of dicumyl peroxide as the free radical generator and 0.5 parts by weight of Flectol H (available from Monsanto) as an antioxidant. The reaction is carried out in a PR46 Buss Ko-Kneader with the heater units set at 200°C/240°C/160°C and the die heater at setting number 7. The material produced is face cut and air cooled at an output rate of 5.2 kg per hour.

#### Example 2

##### One part adhesive composition

The composition is the admixture of the following components:

15	SGSIS <sup>+</sup>	31.3%
	Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
	175°F Micro wax (microcrystalline wax)	20.0%
	Sasol Wax (Fischer Tropsch wax)	10.0%
20	Irganox 1010 (antioxidant)	1.0%
	Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
	Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%

25

+ product of Example 1.

The composition is homogenized prior to the addition of the catalyst. The catalyst is then mixed in and the composition is filled into aluminium cartridges for a hot melt adhesive applicator. A silica gel sachet is placed in the filled cartridge which is then sealed.

The compositions of Examples 3 to 9 are mixed and filled into containers as for Example 2.

Example 3One part adhesive composition

- 5 The composition is the admixture of the following components:

	SGSIS <sup>+</sup>	31.3%
10	Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
	Irganox 1010 (antioxidant)	1.0%
	Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
15	Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
	Hyvis 30 (polybutene - plasticizer)	30.0%

+ As described in Example 1.

20

Example 4One part adhesive composition

- 25 The composition is the admixture of the following components:

	SGSIS <sup>+</sup>	31.3%
	Catalyst/polyethylene blend (1% dibutyl tin dilaurate)	1.7%
30	Irganox 1010 (antioxidant)	1.0%
	Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
	Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
35	Hyvis 30 (polybutene - plasticizer)	30.0%

+ As described in Example 1.

Example 5One part adhesive composition

- 5 The composition is the admixture of the following components:

	SGSIS <sup>+</sup>	31.3%
	Catalyst/SEBS blend (1% dibutyl tin dilaurate)	1.7%
10	Irganox 1010 (antioxidant)	1.0%
	Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
	Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
15	Hyvis 30 (polybutene - plasticizer)	30.0%

+ As described in Example 1.

20 Example 6

One part pressure sensitive adhesive composition

The composition is the admixture of the following components:

25	SGSIS <sup>+</sup>	31.3%
	Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
	Irganox 1010 (antioxidant)	1.0%
30	Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
	Wingtack 10 (liquid polyterpene - tackifying resin)	10.0%
	Hyvis 30 (polybutene - plasticizer)	30.0%

35

+ As described in Example 1.

Example 7One part foamed gasket adhesive composition

The composition is the admixture of the following components:

5		
	SGSIS <sup>+</sup>	31.3%
	Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
10	Irganox 1010 (antioxidant)	1.0%
	Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	10.0%
	Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
15	Shellflex 451 (process oil)	46.0%

+ As described in Example 1.

Example 8One part adhesive composition

The composition is the admixture of the following components:

25		
	SGSIS <sup>+</sup>	31.3%
	Catalyst/polypropylene blend (1% dibutyl tin dilaurate)	1.7%
	Irganox 1010 (antioxidant)	1.0%
	Escorez 5300 (hydrogenated alicyclic hydrocarbon - tackifying resin)	26.0%
30	Piccotex 100 ( $\alpha$ -methyl styrene-vinyl toluene copolymer - tackifying resin)	10.0%
	Hyvis 30 (polybutene - plasticizer)	30.0%

35 + As described in Example 1.



Example 9One part adhesive composition

- 5 The composition is the admixture of the following components:

	SGSIS <sup>+</sup>	31.3%
	Catalyst/polypropylene blend (1% dibutyl	
10	tin dilaurate)	1.7%
	Irganox 1010 (antioxidant)	1.0%
	Escorez 5300 (hydrogenated alicyclic	
	hydrocarbon - tackifying resin)	26.0%
	Piccotex 100 ( $\alpha$ -methyl styrene-vinyl	
15	toluene copolymer - tackifying resin)	10.0%
	Hyvis 30 (polybutene - plasticizer)	10.0%
	PEG 400 (polyethyleneglycol)	20.0%

+ As described in Example 1.

20

Example 10Two composition pressure sensitive adhesive system

The first composition comprises the following components:

25	SGSIS <sup>+</sup>	30 parts
	Wingtack 10 (polyterpene resin)	30 parts
	Irganox 1010 (antioxidant)	0.5 parts

30

+ As described in Example 1.

The second composition comprises the following components:

35	Unitack R100 (rosin ester)	99%
	Dibutyl tin dilaurate	0.017 parts

In use, the first and second compositions are melted, mixed in a weight ratio of 2:1 and the mixture is applied to a substrate.

5

Example 11Solvent based Pressure Sensitive Adhesive

- 100 parts SGsBR++  
10 75 parts Pentalyn H (Pentaerythritol ester of hydrogenated rosin available from Hercules)  
1005 parts Toluene solvent.  
1.75 parts catalyst masterbatch \*
- 15 ++ SGsBR is a silane grafted styrene butadiene rubber (Kraton 1011 available from Shell, 54 Mooney viscosity, 23.5% styrene) prepared analogously to Example 1.
- \* Catalyst masterbatch is prepared as a 1% dispersion of  
20 dibutyl tin dilaurate in an ethylene-vinyl acetate copolymer carrier and is added to give a final catalyst concentration of 0.017% of total solids.

- The polymer, rosin and catalyst masterbatch are  
25 dispersed in the solvent in a Silverson mixer.

Example 12Nitrile Solvent

- 30 20 parts Silane grafted Breox 1442 (Nitrile available from BP)  
80 parts MEK solvent  
0.2 parts catalyst masterbatch (see Example 11)
- 35 The polymer and catalyst masterbatch are dispersed in the solvent in a Silverson mixer.

Example 13Neoprene Contact Adhesive

- 15 parts Silane grafted Neoprene AC (DuPont)  
5 5 parts Nirez 1085 (Reichhold polyterpene)  
80 parts MEK Solvent.  
0.2 parts catalyst masterbatch (see Example 11)

10 The polymer, polyterpene and catalyst masterbatch  
are dispersed in the solvent in a Silverson mixer.

Example 14Butyl Solvent based pressure sensitive

- 15 100 parts SG-butyl<sup>++</sup> (Butyl 065 available from EXXON)  
35 parts Herculyn (Hercules rosin ester)  
45 parts Escorez 1315 (EXXON hydrocarbon resin)  
70 parts Polybutene H-100 plasticiser  
1000 parts Heptane Solvent  
20 2.5 parts catalyst masterbatch (see Example 11)

<sup>++</sup> Silane grafted butyl rubber which may be prepared analogously to Example 1.

- 25 Polymer, resins, plasticiser and catalyst masterbatch  
are dispersed in the solvent in a Silverson mixer.

Example 15SBR based sealant

- 30 12 parts SG-SBR<sup>++</sup> (Kraton 1011 available from Shell)  
19 parts stabilised rosin (Staybelite available from Hercules)  
4 parts plasticiser (Shellflex 451)  
35 17 parts soft clay  
10 parts fibrous talc  
26 parts Toluene

12 parts Xylene

0.6 parts catalyst masterbatch (see Example 11)

5 ++ A silane grafted styrene-butadiene rubber which may be prepared analogously to Example 1.

The fillers are mixed with the rubber in a Brabender internal mixer, chopped and then added to the resin, plasticiser, solvents and catalyst masterbatch in a  
10 Silverson mixer.

Example 16

Neoprene based sealant

15 100 parts silane grafted Neoprene AC

100 parts Calcium Carbonate

35 parts Nirez 1085 resin

80 parts solvent of composition 5 parts Hexane

3 parts MEK

20 2 parts Toluene

2.5 parts of catalyst masterbatch (see Example 11)

The filler is mixed with the rubber in a Brabender internal mixer, chopped and then added to the resin,  
25 solvent and catalyst masterbatch in a Silverson mixer.

Example 17

Butyl based sealant

30 12% SG EXXON Butyl 065<sup>++</sup>

29% Fibrous talc

20% Calcium Carbonate Whiting

3% Titanium Dioxide

4% Nirez 1085

35 14% Polybutene H-300

15% Mineral spirits

2% Cab-O-Sil

1% Catalyst masterbatch (see Example 11)

++ A silane grafted butyl rubber which may be prepared analogously to Example 1.

5

The fillers are mixed with the rubber in a Brabender internal mixer, chopped and then added to the resin, plasticiser, solvents and catalyst masterbatch in a Silver'son mixer.

10

Example 18

Tyre tread

100 parts SG-SBR\*\* (1507 available from Shell)

15 65 parts Carbon black

1.5 parts catalyst masterbatch (see Example 11)

++ A silane grafted styrene-butadiene rubber which may be prepared analogously to Example 1.

20

Ingredients are mixed in an internal mixer and formed to shape by conventional injection or compression moulding.

Example 19

25 Inner tubes

100 parts SG Butyl\*

25 parts process oil

30 parts Carbon Black SRF

30 30 parts Carbon Black FEF

2 parts catalyst masterbatch (see Example 10)

+ A silane grafted butyl rubber which may be prepared analogously to Example 1.

35

Ingredients are mixed in an internal mixer and formed to shape by conventional injection or compression moulding.

Example 20SBR based shoe soles

- 100 parts SG-SBR<sup>++</sup> (1507 available from Shell)  
5 40 parts Silica  
10 parts Light process oil  
1.5 parts catalyst masterbatch (see Example 11)

- ++ A silane grafted styrene-butadiene rubber which may  
10 be prepared analogously to Example 1.

Ingredients are mixed in an internal mixer and formed to shape by conventional injection or compression moulding.

15 Example 21Neoprene oil resistant shoe soles

- 100 parts silane grafted Neoprene W (DuPont)  
90 parts Carbon Black SRF  
20 15 parts Light process oil  
2 parts catalyst masterbatch (see Example 11)

- Ingredients are mixed in an internal mixer and formed to shape by conventional injection or compression moulding.  
25

Example 22Nitrile based shoe soles

- 80 parts SG-Nitrile<sup>++</sup> (Chemigum N600 available from  
30 Goodyear Tyre and Rubber)  
20 parts SG-SBR 1502<sup>++</sup> (Shell)  
60 parts silica  
10 parts Staybelite resin  
20 parts Light process oil  
35 2 parts catalyst masterbatch (see Example 11)

++ These may be silane grafted analogously to Example 1.

Ingredients are mixed in an internal mixer and formed to shape by conventional injection or compression moulding.

CLAIMS

1. A silane-modified polymer having unsaturated carbon-carbon bonds situated along the polymer backbone or in groups pendant therefrom.
2. A silane-modified polymer as claimed in claim 1 wherein from 0.5 to 50% of the carbon-carbon bonds in the polymer backbone or a block thereof, or in groups pendant therefrom, are carbon-carbon double bonds.
3. A silane-modified polymer as claimed in claim 2 wherein from 1% to 35% of the carbon-carbon bonds are carbon-carbon double bonds.
4. A silane-modified polymer as claimed in any preceding claim wherein the polymer is a styrene-butadiene-styrene block copolymer, a styrene-butadiene random copolymer, a nitrile rubber, a polychloroprene or a butyl rubber.
5. A silane-modified styrene-isoprene-styrene block copolymer as claimed in any of claims 1 to 3.
6. A silane-modified polymer as claimed in any preceding claim wherein the silane side chain is of formula (I)
- $$\text{-A-Si(R)}_{3-m}\text{(X)}_m \quad (\text{I})$$

wherein A represents an optionally substituted divalent organic radical; X represents a leaving group displaceable by hydrolysis; m is 1, 2 or 3; and R represents a blocking group not displaceable by hydrolysis.

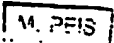


7. A silane-modified polymer as claimed in claim 6  
obtained by grafting with vinyl trimethoxy silane,  
vinyl triethoxy silane or gamma-  
methacryloyloxypropyl trimethoxy silane.
- 5
8. Articles formed from a cross-linked silane-modified  
polymer as claimed in any preceding claim.
9. An adhesive composition comprising a silane-  
modified polymer as claimed in any of claims 1 to 7  
and a catalyst for the condensation of said  
polymer.
- 10
10. An adhesive composition as claimed in claim 9  
applicable in hot melt form.
- 15
11. A hot melt adhesive composition as claimed in claim  
10 comprising a silane-modified styrene-isoprene-  
styrene block copolymer.
- 20
12. A hot melt adhesive composition as claimed in claim  
10 or 11 which further comprises a plasticiser.
13. A hot melt adhesive composition as claimed in any  
of claims 10 to 12 comprising at least one further  
component selected from antioxidants; tackifying  
resins; further polymers; and diluents and  
modifiers.
- 25
14. A hot melt adhesive composition as claimed in any  
of claims 10 to 13 wherein the silane-modified  
polymer forms from 10 to 40% by weight of the  
composition.
- 30
15. A hot melt adhesive composition as claimed in any  
of claims 10 to 14 further comprising a moisture  
releasing agent.
- 35

16. A hot melt adhesive system comprising a first composition comprising a silane-modified polymer as claimed in any of claims 1 to 7 and a second composition comprising a catalyst for the condensation of said silane-modified polymer, said first and second compositions being packed in separate containers.
17. A hot melt adhesive applicator cartridge comprising a water-tight container containing therein a desiccant and a hot-melt adhesive composition, said composition comprising a silane-modified polymer as claimed in any of claims 1 to 7 and a catalyst for the condensation thereof.
18. Use of an adhesive composition or system as claimed in any of claims 10 to 16 in product assembly.
19. A pressure sensitive adhesive composition, characterised in that it contains a cross-linkable silane-modified polymer as claimed in any of claims 1 to 7.
20. A pressure sensitive adhesive composition scoring greater than 1 N/25mm in the loop tack (FTM No 9) test and comprising an adhesive composition as claimed in claim 19 cured to effect cross linking of said silane-modified polymer.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 90/01675

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: C 08 F 8/42, C 09 J 109/00, C 09 J 125/10, C 09 J 153/02		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC5	C 08 F; C 09 J	
Documentation Searched other than Minimum Documentation to the extent that such documents are included in fields searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
P, Y	WO, A1, 8911512 (SWIFT ADHESIVES LIMITED) 30 November 1989, see inter alia page 5, last paragraph claims 1,12,13,17-21  --	1-7,9-10
Y	EP, A2, 0240044 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 7 October 1987, see inter alia abstract, page 3, line 40 - page 4, line 6  --	1-7
Y	Dialog Information Services, File 351, World Patent Index 81-91, Dialog accession no. 84-1848101/30, Hitachi Cable KK: "Mfg. crosslinked moulding for cable insulation etc. by reacting silane cpd. with styrene block copolymer, mixing with condensn. cata- lyst etc.", JP 59102931, A, 840614, 8430 (Basic)  --	1-7
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
25th January 1991	19. 02. 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 M. PEIS	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	Dialog Information Services, File 351, World Patent Index 81-91, Dialog accession no. 83-761817/37, Mitsubishi Petroch KK: "Heat distortion resistant crosslinking compsn. obtd. by modifying hydrogenated block copolymer compsn. with unsatd. silane for high flexibility etc.", JP 58132032, A, 830806, 8337 (Basic)	1-7
Y	Chemical Abstracts, volume 105, no. 8, 25 August 1986, (Columbus, Ohio, US), see page 60, abstract 61816d, & JP,, 6142582 ((Japan Synthetic Rubber Co.,Ltd.)) 1986	1-4,9-10
Y	Chemical Abstracts, volume 79, no. 10, 10 September 1973, (Columbus, Ohio, US), see page 58, abstract 54541b, & JP,, 7339537 ((Asahi Chemical Industry Co.,Ltd.)) 1973	1-4,9-10
A	EP, A1, 0171225 (JAPAN SYNTHETIC RUBBER CO.,LTD.) 12 February 1986; see the whole document	1-20

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.PCT/GB 90/01675**

SA 41474

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on 28/12/90  
The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 8911512	30/11/89	WO-A- 89/11513	30/11/89
EP-A2- 0240044	07/10/87	AU-B- 589744	19/10/89
		AU-D- 6929387	03/09/87
		CA-A- 1269466	22/05/90
		JP-A- 62218468	25/09/87
		US-A- 4783504	08/11/88
EP-A1- 0171225	12/02/86	JP-A- 61171714	02/08/86

For more details about this annex : see Official Journal of the European patent Office, No. 12/82

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